

4132 *

CHAPTER 3

LIPID AND OTHER NONPETROCHEMICAL RAW MATERIALS

Frank Scholnick

Eastern Regional Research Center
U.S. Department of Agriculture
Philadelphia, Pennsylvania

I. INTRODUCTION	87
II. SOURCES	88
A. Carboxylic Acids	88
B. Lignosulfonates	98
C. Natural Fats and Oils	98
D. Fatty Alcohols	101
III. CHEMICAL MODIFICATIONS OF NONPETROCHEMICAL RAW MATERIALS	104
A. Esters and Ether-Esters	104
B. Nitrogen Derivatives	106
REFERENCES	107

I. INTRODUCTION

Anionic surfactants are principally synthesized either from petroleum or from lipid and nonpetrochemical raw materials. The first source has been discussed in Chapter 2. Although petroleum derivatives continue to be a very important source of anionic synthetic detergents, considerable quantities of the latter have also been prepared from many naturally occurring fats and oils.

In 1973, U.S. production of anionic surfactants approached 3.0 billion lb. Of this total, as shown in Table 1, almost 1.7 billion lb were obtained

TABLE 1
U.S. Production of Nonpetrochemical Surface-Active Agents, 1973

Anionic surface-active agent	Production, 1000 lb
Fatty, rosin, and tall-oil acids and their salts	939,159
Sulfonic acids and salts	
Lignosulfonates, total Ca, NH ₄ , Na salts	689,495
Sulfosuccinic acid amides and esters	19,490 ^a
Taurine derivatives	3,504 ^a
Sulfuric acid esters and their salts	
Sulfated natural fats and oils	31,853
Sulfated fatty and tall-oil acids, amides, and esters	8,251
Sulfated linear alcohols	835 ^a
Phosphoric acid esters of linear alcohols	3,955 ^a
Total	1,696,542

^aProbably includes some petroleum-based substrates.

from nonpetrochemical sources such as (1) potassium and sodium salts of fatty, rosin, and tall-oil acids; (2) calcium, ammonium, and sodium salts of lignosulfonates; (3) sulfated fatty and tall-oil acids and their derivatives; (4) sulfated fatty and sperm-oil alcohols; and (5) sulfated natural fats and oils [1]. Each of these raw materials is an important source for anionic surfactants and will be discussed below.

II. SOURCES

A. Carboxylic Acids

1. Fatty Acids

In 1973, almost 690 million pounds of potassium and sodium salts of fatty acids from animal and vegetable sources were produced for use as anionic surface-active agents. Some of the production figures are listed in Table 2 [1].

These fatty acids are obtained from the glycerides present in natural fats and oils (see Sec. C). The fatty acids of natural fats have almost always an even number of carbon atoms ranging from 4 to 24 and may be saturated, monounsaturated, or polyunsaturated. The unsaturation is usually of the cis

TABLE 2
U.S. Production of Salts of Fatty Acids, 1973

Potassium and sodium salts	Production, 1000 lb
Acids	
Coconut oil	149,601
Corn oil	782
Mixed vegetable oil fatty	3,109
Oleic	1,450
Soybean oil	579
Stearic	1,750
Tallow	528,151
Total	685,422

type. Fatty acids are particularly suitable for the production of surface-active agents, especially those acids containing 12 to 18 carbon atoms, such as lauric, myristic, palmitic, stearic, oleic, and ricinoleic acid. Highly unsaturated acids are subject to oxidation and rancidity, thus limiting their usefulness. Table 3 gives the fatty acid composition of selected animal and vegetable fats and oils.

The fatty acids are prepared from the glyceride fat or oil by several processes involving either saponification followed by acidification, or hydrolysis with or without a catalyst. Most of the soap produced throughout the world is prepared by batch saponification or by continuous processes [2]. The details of soap manufacture will not be covered here. In the United States hydrolysis of glycerides to prepare fatty acids is most commonly effected by a continuous, countercurrent, high-temperature, and pressure process. The crude product is purified by fractional crystallization [3], especially where unsaturation is a factor, or by distillation [4]. Some of the physical properties of fatty acids are given in Table 4. Their chemical reactions used in preparation of anionic surfactants will be discussed in Sec. III.

2. Tall-Oil Fatty and Rosin Acids

These acids occur in nature in pine wood as esters of glycerol or sterols. In the sulfate process for making paper pulp from pine wood, most of the esters are saponified to form salts of the fatty and rosin acids. In 1973, over 28 million lb of potassium and sodium salts of tall-oil acids were produced [1]. Acidification of the soaps obtained by saponification furnishes crude tall oil containing an approximately equal mixture of fatty and rosin acids contaminated

Fatty Acid Composition of Selected Fats and Oils, %

[illegible]

TABLE 4
Physical Properties of Fatty Acids

Acid	Titer, ° C	Value			Unsaponifiable, %
		Acid	Saponification	Iodine	
Lauric, %					
94/96	39-41	279-284	279-284	0.5 ^b	0.5
98/100	43-43.6	279-282	279-282	0.2 ^b	0.2
Stripped coconut oil	25-28	250-260	252-262	8-14	0.5
Stripped palm-kernel oil ^a	23-27	250-260	250-260	16-22	1.0
Myristic, %					
94/96	50-53	244-254	245-255	1.0 ^b	0.5
98/100	51-54	244-254	245-255	1.0 ^b	0.5
Palmitic, %					
94/96	60-61	215-225	215-225	2.0 ^b	0.5
98/100	61-62	219-224	219-224	2.0 ^b	0.5
Stearic, %					
94/96	64-66	195-198	196-199	1-3	1.5
98/100	66-68	195-199	196-200	2.0 ^b	1.5
Stearin, pressed					
single	52-53	207-211	207-211	8-10	0.5
double	53-54	208-211	208-211	5-8	0.5
triple	54-56	207-211	207-211	1.5-5	0.5 ^b

TABLE 4 (Continued)

Acid	Titer, °C	Value			Unsaponifiable, %
		Acid	Saponification	Iodine	
Tallow ^a	39-43	204-208	205-209	53-57	1.5 ^b
Oleine light colored	7-10	186-204	188-206	85-92	2-6
Palm oil ^a	42-46	207-213	209-215	44-54	1.5 ^b
Refined tall oil ^a	--	163-168	165-170	153-167	7-8.0
light colored	--	188-193	190-195	155-165	1.5-2.2

Source: Ref. 5, p. 123. Courtesy, Chemical Rubber Publishing Co., Cleveland, Ohio.

^aDistilled.

^bMaximum.

with about 10% neutral materials (polycyclic hydrocarbons, sterols, and high-molecular-weight alcohols). The composition of some crude tall oils is given in Table 5.

Distillation of crude tall oil yields a product having the composition and properties given in Table 6, while tall oil refined by treatment with concentrated sulfuric acid has the composition and properties shown in Table 7.

Detailed descriptions are available of the processing and refining of tall oil in Refs. 6 and 7. Fractional distillation effects a good separation of the rosin and fatty acids. A typical composition of commercial tall-oil fatty acids is given in Table 8. It is evident that oleic and linoleic acids are the principal fatty acids found in low-rosin tall oil. Some of the properties of the tall oil fatty acids are given in Table 9.

TABLE 5
Composition of Some Crude Tall Oils

Pine-tree source	Fatty acids, %	Rosin acids, %	Neutral fraction, %
Swedish	40-58	30-50	6-15
Finnish	37-59	32-49	6.8-11.3
Finnish (whole trees)	29-36	52-57	9-11
Finnish (sawmill waste)	49-62	30-39	5-12
Danish	50	43	6.7
American	18-53	35-65	8-24
Canadian mixed sample	46	28	25
S.E. Virginian	55-56	39-40	4.8-5.8
N.E. North Carolinan	53-54	40-41	5.3-6.1
S.W. North Carolinan	51-53	41-42	6.1-6.9
E. Central S. Carolinan	46-48	45-47	6.2-7.4
E. Central Georgian	45-48	45-48	6.2-7.4
S.E. Georgian	43-46	47-51	6.3-7.4
S.E. Texas	45-48	46-48	5.3-7.1

Source: Ref. 6, p. 617. Courtesy, John Wiley & Sons, Inc., New York.

The composition and properties of rosin obtained by fractionation of crude tall oil are listed in Table 10.

TABLE 6
Distilled Tall Oil, Composition and Properties

Average composition, %		Typical properties	
Fatty acids	60-85	Color, Gardner	4-12
Rosin	14-37	Specific gravity, 25° C (77°F)	0.940-0.950
Neutral materials	1-3	Acid number	180-190
		Saponification number	185-195
		Viscosity (Gardner-Holdt)	B-E
		Flash point (open cut)	
		° C	182-210
		° F	360-410

Source: Ref. 6, p. 617. Courtesy, John Wiley & Sons, Inc., New York.

TABLE 7
Acid-Refined Tall Oil, Composition and Properties

Average composition, %		Typical properties	
Fatty acids	50-70	Color, Gardner	8-12
Rosin	25-42	Specific gravity, 25° C (77°F)	0.900-1.000
Neutral materials	5-7	Acid number	155-170
		Saponification number	160-175
		Viscosity (Gardner-Holdt)	Z-Z ₂
		Flash point (open cup)	
		° C	204-216
		° F	400-420

Source: Ref. 6, p. 620. Courtesy, John Wiley & Sons, Inc., New York.

The major carboxylic acids found in tall-oil rosin are derivatives of alkyl hydrophenanthrene. Typical formulas and percentages are given in Table 11.

TABLE 8
Typical Composition of Tall Oil Fatty Acids in Low-Rosin Tall Oil

Fatty acid	Percent in low-rosin tall oil
Palmitic	1
Palmitoleic	--
Stearic	2
Oleic	51
Linoleic (nonconjugated)	40
Linoleic (conjugated)	5
Unknown	4

Source: Ref. 7, p. 26. Courtesy, Pulp Chemicals Association, New York.

TABLE 9
Properties of Commercial-Type Tall-Oil Fatty Acids

Property	Type Ia ^a		Type II ^a		Type III ^a	
	Min	Max	Min	Max	Min	Max
Acid number	197		192		190	
Rosin acids, %		1.0		2.0		10.0
Neutral materials, %		1.0		2.0		10.0
Fatty acids, %	98		96		90	
Color, Gardner		4		5		10.0
Iodine number	125	135				

Source: Ref. 6, p. 621. Courtesy, John Wiley & Sons, Inc., New York.

^aGrouped by rosin content.

TABLE 10
Tall-Oil Rosin, Composition and Properties

Average composition, %		Typical properties	
Rosin acids	90-95	Color, USDA rosin scale	X-N
Fatty acids	2-3	Acid number	162-172
Neutral materials	3-7	Saponification number	170-180
		Softening point	
		° C	73-83
		° F	163-181

Source: Ref. 6, p. 619. Courtesy, John Wiley & Sons, Inc., New York.

TABLE 11
Principal Resin Acids Found in Tall Oil Rosin

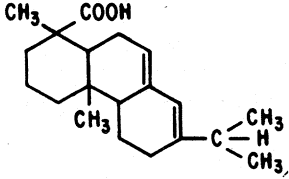
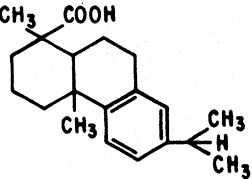
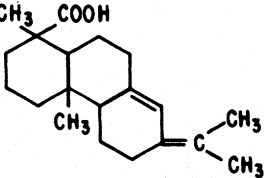
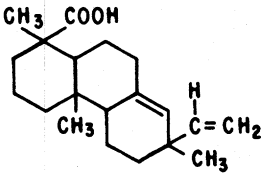
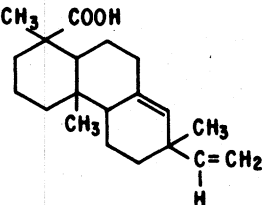
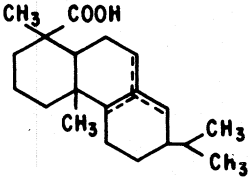
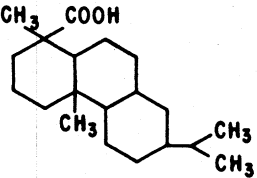
Component	Structure	Approximate percentage
Abietic acid		30-40
Dehydroabietic acid		5
Neoabietic acid		10-20

TABLE 11 (Continued)

Component	Structure	Approximate percentage
Dextropimaric acid		8
Isodextropimaric acid		8
Dihydroabietic acid		14
Tetrahydroabietic acid		14

Source: Ref. 6, p. 626, and Ref. 7, p. 33. Courtesy, John Wiley & Sons, Inc., New York, and Pulp Chemicals Association, New York, respectively.

Reactions of carboxylic acids found in tall oil will be discussed subsequently; however, mention should be made of their neutralization. Water-soluble soaps of tall-oil fatty acids are prepared by neutralization of these acids with sodium, potassium, or ammonium hydroxide. Oil-soluble "metallic" soaps can be prepared by treating water-soluble soaps with an appropriate magnesium, aluminum, or calcium salt. Rosin acids form similar salts or soaps although the carboxyl group is somewhat sluggish to react because of the bulkiness of the groups attached to it. Other chemical reactions are described in Sec. II.

B. Lignosulfonates

Sulfonates prepared from lignin are an important source of anionic surfactants (see Table 1). They are prepared from coniferous (soft) and deciduous (hard) varieties of wood, as well as various other plants. The lignin content of these woods depends upon the source and location of the tree and on the age of the plants. Tables 12 and 13 list the lignin content of various woods and plants. Lignin is believed to be a complex system of polymers derived from 4-hydroxyphenylpropane and related compounds [8]. Sulfonates of lignin are formed when wood chips are heated at 125-145°C under pressure with a bisulfite (usually calcium bisulfite) and sulfur dioxide. Over half of the wood is dissolved forming soluble lignosulfonic acids and salts. Insoluble basic calcium salts are prepared by addition of calcium hydroxide. These salts can be separated and converted to other appropriate derivatives particularly effective as dispersing agents of carbon in aqueous systems.

C. Natural Fats and Oils

In 1973, almost 32 million lb of natural fats and oils were sulfated for use as anionic surfactants. The natural fats were obtained from vegetable sources

TABLE 12
Lignin Content of Some Varieties of North American Wood

Coniferous	Percent ^a	Deciduous	Percent
Douglas fir	27.2	Beech	21.0
Noble fir	29.3	Trembling aspen	19.3
Englemann spruce	26.3	White birch	20.0
Jack pine	26.7	Yellow birch	22.7
Slash pine	28.0	Chestnut oak	24.3
Western hemlock	27.8	Red maple	22.8

Source: Ref. 9, p. 368. Courtesy, John Wiley & Sons, Inc., New York.

^aLignin as percentage of dry unextracted wood.

TABLE 13
Lignin in Miscellaneous Plant Materials

Source	Percent	Source	Percent
Spruce wood (normal)	26	Rice hulls	40.0
Spruce wood (compression)	38	Peanut shells	28.0
Eucalyptus (normal)	22	Bune from flax	24.4
Eucalyptus (tension)	16	Barley straw	16-22
Loblolly pine (early sapwood)	28.1	Bagasse	20.3
Loblolly pine (late sapwood)	26.8	Coconut shells	31.9
Loblolly pine (early heartwood)	26.8	Oat straw	14-22
Loblolly pine (late heartwood)	24.2	Clover	4.8
Black spruce bark (outer)	33.9	Hay	7.3
Black spruce bark (inner)	6.6	Alfalfa	23
Black spruce (cambium)	1.8	Club moss	37
Jute	14.2	Peat moss	4.5
Jute sticks	19.6	Flax straw	21.8
Bamboo	29-35	Pine needles	23.9
		Wheat straw	13.9
		Corncoobs	13.4

Source: Ref. 9, p. 368. Courtesy, John Wiley & Sons, Inc., New York.

such as castor, coconut, and soybean oil, from mixed fish oils, cod and sperm oil, and from animal sources including tallow and neatsfoot oil. Production figures for 1973 [1] are listed in Table 14. Statistics are not available regarding the production of other sulfated natural fats and oils, including mustard seed, peanut, ricebran, herring, and whale oil, and lard and grease although their use has been reported [1].

The technology concerned with separation of fats and oils from their natural sources is extensive and highly specialized [10]. Oils from animal tissues are extracted by means of heat treatment or "rendering." Two general methods of rendering exist. In "dry" rendering the animal material is cooked with agitation at atmospheric, high, or reduced pressures. In "wet" rendering, often used in extraction of lard, tallow and whale oil, the fat is heated in the presence of water or with steam. Vegetable oil seeds are

TABLE 14
U.S. Production of Sulfated Natural Fats and Oils, 1973

Sulfated natural fats and oils, sodium salt	Production, 1000 lb
Castor	5,920
Coconut	871
Cod	1,666
Herring	690
Mixed fish	4,023
Neatsfoot	2,066
Ricebran	9
Soybean	614
Sperm	778
Tallow	5,860
All other	9,356
Total	31,853

cleaned, dehulled, and reduced in size before they are pressed or extracted with solvents.

As previously discussed, fats and oils are usually complex mixtures of glycerides of fatty acids. The esters are randomly distributed between the 1- and 2-positions of glycerol and their location can affect the physical properties such as melting point and crystal structure of the fats. To a minor extent, mono- and diglycerides exist in natural fats and result in the presence of free hydroxyl groups. For detailed discussions and description of the glyceride composition of animal and vegetable fats, see Ref. 11. The composition of some selected fats and oils is given in Table 3.

In contrast with most fats and oils, sperm oil is a mixture of esters of fatty acids bound mainly to higher fatty alcohols rather than glycerol. Industrial sperm oil is obtained from both the blubber and head cavities of the sperm whale. Hilditch [12] reported sperm-head oil to consist of 74% of fatty esters and 26% of triglycerides, while blubber oil contained 66 and 34%, respectively, of these components. The fatty acid and alcohol composition of the oils obtained from sperm whales was determined by the same workers [13] and is given in Table 15 and 16. The preparation of long-chain alcohols from sperm oil and other sources will be discussed in Sec. D.

TABLE 15
Weight Percent of Fatty Acid Components of Sperm Whale
Head and Blubber Oils

Acid	Weight %	
	Head oil	Blubber oil
Saturated		
Decanoic	3.5	--
Lauric	16	1
Myristic	14	5
Palmitic	8	6.5
Stearic	2	--
Unsaturated		
C ₁₂	4 (-2H) ^a	--
C ₁₄	14 (-2H)	4 (-2H)
C ₁₆	15 (-2H)	26.5 (-2H)
C ₁₈	17 (-2H)	37 (-2H)
C ₂₀	6.5 (-2H)	19 (-2.5H)
C ₂₂	--	1 (-4H)

Source: Ref. 12, p. 72. Courtesy, John Wiley & Sons, Inc., New York.

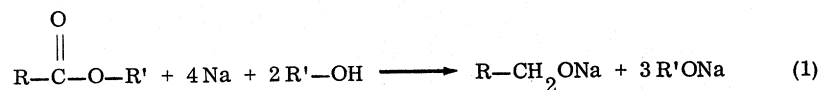
^aDenotes double bond.

During sulfation of natural fats and oils, sulfuric acid attacks the carbon-carbon double bonds and leads to formation of sulfates, $R-CH_2-CH(OSO_2Na)-R'$, as well as some by-products caused by hydrolysis or formation of lactones, lactides, and polymers. Completely saturated fatty acid chains are for the most part unaffected. Where hydroxyl groups are present, as in castor oil or in monoglycerides, sulfation of these functional groups occurs to yield esters. These types of surfactants are discussed in Chapter 7.

D. Fatty Alcohols

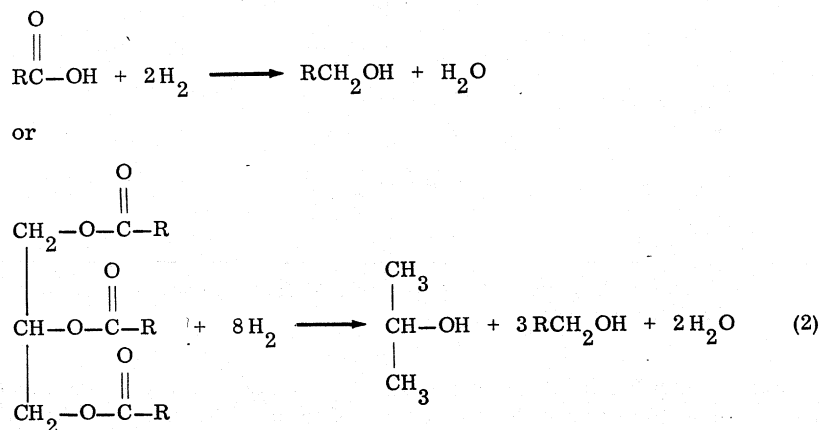
Unlike fatty acids, aliphatic alcohols are not found in large quantities in nature. However, both cetyl and oleyl alcohols make up a significant portion of the component alcohols found in sperm oil (see Table 16). In general, the fatty alcohols are obtained from the oil by saponification and are purified by crystallization procedures similar to those used for fatty acids.

In order to supplement the quantities of fatty alcohols available from natural sources, the Bouveault-Blanc method of reduction of esters using sodium and a lower alcohol was extended to glycerides. Thus C_{12} - C_{16} alcohols were obtained from coconut and palm kernel oils and C_{16} - C_{18} alcohols from tallow. The process has been described by Schroeder [14]. The overall reaction is shown in Eq. (1):



Isolated or nonconjugated double bonds are unaffected.

High-pressure catalytic hydrogenation has been used with fatty acids, their lower esters, or their glycerides [15]. The reaction is carried out at 200 to 250 atm at about 300°C , usually using copper chromite as catalyst, as shown in Eq. (2):



The reaction is nonselective and causes hydrogenation of double bonds and formation of saturated alcohols. Other methods for catalytic reduction of animal fats to yield unsaturated alcohols such as oleyl alcohol have been studied [16, 17]. Yields of 60-70% of oleyl alcohol from red-oil grade oleic acid have been reported recently using a mixed catalyst systems of Cr-Zn-Cd-Al at 350°C and 3000 psi [18].

Some of the properties of commercial fatty alcohols obtained by high-pressure hydrogenation of fats and oils are given in Tables 17 and 18. Preparation of higher alcohols from petrochemical sources has been discussed in Chapter 2. The alcohols, natural or synthetic, find wide use in the preparation of anionic detergents such as alcohol sulfates and sulfates of ethylene oxide adducts of the alcohols. The synthesis of these surfactants will be described in a subsequent chapter.

TABLE 16
Weight Percent of Fatty Alcohol Components of Sperm Whale
Head and Blubber Oils

Alcohol	Weight %	
	Head oil	Blubber oil
Saturated		
C ₁₄ Tetradecyl	8	--
C ₁₆ Hexadecyl (cetyl)	44	25
C ₁₈ Octadecyl	6	1
Unsaturated		
C ₁₆ Hexadecenyl	4	--
C ₁₈ Octadecenyl (oleyl)	28	66
C ₂₀ Eicosenyl	10	8

Source: Ref. 12, p. 73. Courtesy, John Wiley & Sons, Inc., New York.

TABLE 17
Properties of Pure Fatty Alcohols

Alcohol	Formula	Molecular weight	Melting point, °C	Boiling point, °C	Hydroxyl number
Decanol	C ₁₀ H ₂₁ OH	158	7	231 ⁷⁶⁰	355
Undecanol	C ₁₁ H ₂₃ OH	172	14	131 ¹⁵	326
Dodecanol (lauryl)	C ₁₂ H ₂₅ OH	186	24	135-137 ¹⁰	301
Tridecanol	C ₁₃ H ₂₇ OH	200	30	155 ¹³	280
Tetradecanol (myristic)	C ₁₄ H ₂₉ OH	214	38	159-161 ¹⁰	262
Pentadecanol	C ₁₅ H ₃₁ OH	228	44		246
Hexadecanol (palmitic or cetyl)	C ₁₆ H ₃₃ OH	242	49	179-182 ¹²	232
Heptadecanol	C ₁₇ H ₃₅ OH	256	54		219
Octadecanol (stearyl)	C ₁₈ H ₃₇ OH	270	58	202 ¹⁰	208
Octadecanol (oleyl)	C ₁₈ H ₃₅ OH	268	15-16	177-183 ³	209

Source: Ref. 5, p. 73. Courtesy, Chemical Rubber Publishing Co., Cleveland, Ohio.

TABLE 18
Properties of Typical Commercial Fatty Alcohols
Derived from Oils and Fats

Alcohol	Number of carbons	Iodine number	Solidification point, °C	Boiling range, ^a °C	Hydroxyl number
Lauryl					
Wide-range	C ₁₀ -C ₁₈	<0.5	17-21	220-320	275-285
80% C ₁₂	C ₁₂ -C ₁₄	<0.5	17-23	255-85	283-293
Myristyl,					
95% C ₁₄	C ₁₄	<0.5	36-38	280-95	255-62
Cetyl,					
95% C ₁₆	C ₁₆	<0.5	46-49	316-30	225-35
Stearyl,					
95% C ₁₈	C ₁₈	<0.5	55-57	340-55	203-10
Tallow fatty	C ₁₄ -C ₁₈	<0.5	48-52	120-90	210-20
Oleyl-cetyl mixture	Mainly C ₁₈ ^b	45-120	4-35	310-65	200-20

Source: Ref. 5, p. 72. Courtesy, Chemical Rubber Publishing Co.,
Cleveland, Ohio.

^aAt 760 mm Hg.

^bSaturated and unsaturated.

III. CHEMICAL MODIFICATIONS OF NONPETROCHEMICAL RAW MATERIALS

A few of the reactions necessary to convert nonpetrochemical raw materials into anionic surfactants have been alluded to in the previous part of this chapter. These have included saponification of fats and oils, sulfation of naturally occurring materials, and sulfation of fatty alcohols obtained by reduction or hydrogenolysis of glycerides and fatty acids. Other modifications will now be presented. Several of these reactions will be discussed in depth in later chapters.

A. Esters and Ether-Esters

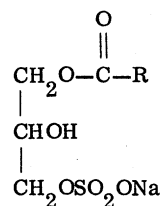
The formation of long-chain esters has been amply documented [19]. Their sulfated derivatives are important anionic surfactants. Some of the various types of esters are briefly described below.

1. Sulfated Esters

Esters of low-molecular-weight alcohols and oleic or ricinoleic acid yield anionic surfactants when sulfated. In 1973, over 4.7 million lb of sulfated oleic acid esters were produced [1]. They are itemized in Table 19.

2. Sulfated Monoglycerides

These materials are prepared by sulfation of monoglycerides [20, 21] and ideally have the structure:



The monoglycerides are usually synthesized by direct esterification of glycerol with a fatty acid, although other methods have been used [22]. A complete discussion follows in Chaps. 6 and 7.

3. Esters of Isothionic Acid (Igepon A)

These esters are prepared by the reaction of fatty acids with sodium isothionate, using an acidic catalyst [23], as shown in Eq. (3):

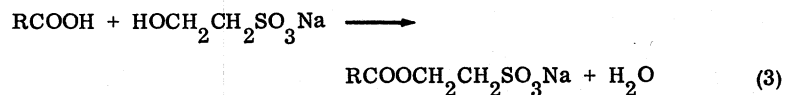
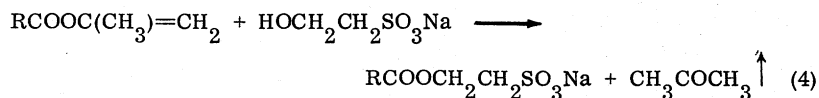


TABLE 19

U.S. Production of Sulfated Esters of Oleic Acid, 1973

Sulfated oleate, sodium salt	Production, 1000 lb
Butyl	1,458
Propyl	517
Others	2,784
Total	4,759

More recently, Bistline and co-workers [24] have used isopropenyl stearate as acylating agent for sodium isothionate at 200° C, see Eq. (4). Yields of 95% were reported.



4. Sulfated Ethylene Oxide Derivatives

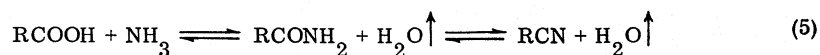
The reaction of ethylene oxide with long-chain acids, alcohols, etc., has been extensively studied [25, 26]. The ethoxylated materials, particularly of higher alcohols, give products with properties resembling those of fatty alcohol sulfates [27].

B. Nitrogen Derivatives

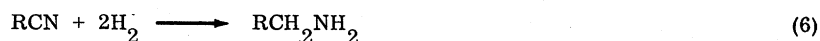
Nonpetrochemical raw materials, principally long-chain acids, are used to prepare nitrogen-containing derivatives. Although the latter are of particular importance in synthesis of cationic surfactants [28], they can be useful starting materials for preparation of anionics.

1. Fatty nitriles and amines

Fatty nitriles are obtained industrially by the reaction of fatty acids with ammonia in a counter-current apparatus at 280–330° C under pressures of 100 psi [29, 30], as shown in Eq. (5).



Reduction of nitriles using a Raney nickel catalyst results in formation of the corresponding amine, see Eq. (6).

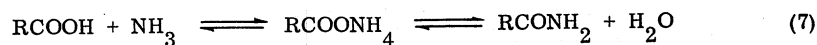


Special conditions are necessary to avoid reduction of double bonds during the hydrogenation with Raney nickel [31].

2. Fatty Amides

a. Simple Amides

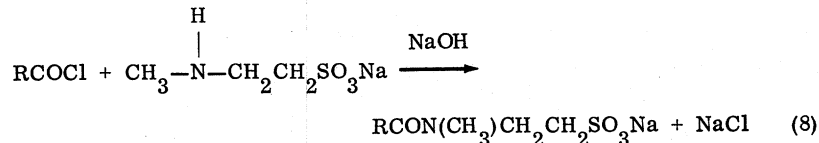
Simple amides of fatty acids are produced in an autoclave by heating the acid with ammonia at about 200° C. Water and ammonia are removed continuously, see Eq. (7).



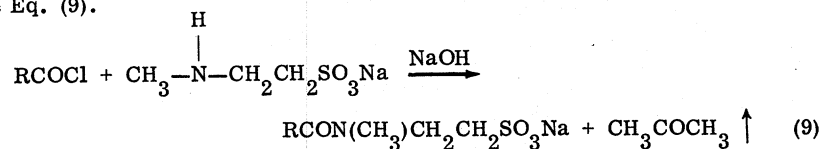
Addition of alkylene oxides and subsequent sulfation will be discussed in Chaps. 6 and 7.

b. Taurine Derivatives

Fatty amides of N-methyltaurine have been synthesized from oleoyl chloride and methyltaurine using the Schotten-Baumann technique, see Eq. (8).



The use of isopropenyl stearate as acylating agent for N-methyltaurine has been reported and leads to formation of acetone as a volatile byproduct [24], see Eq. (9).



c. Derivatives of Amino Acids and Proteins

Acylated amino acids and proteins have been shown to possess surface activity and continue to grow in importance. Over 4.5 million lb of salts of N-lauroylsarcosine, $\text{C}_{11}\text{H}_{23}\text{CON}(\text{CH}_3)\text{CH}_2\text{COONa}$, were produced in 1973 [1]. Coconut fatty acid and oleic acid or their acid chlorides have been reported to convert low-molecular-weight proteins from casein or leather into surfactants [32]. These types of surfactants are discussed in Chap. 16.

REFERENCES

1. United States Tariff Commission, Synthetic Organic Chemicals, United States Production and Sales, 1973. T. C. Publication 728, U.S. Government Printing Office, 1975.
2. R. H. Potts and V. J. Muckerheide, in Fatty Acids and Their Industrial Applications (E. S. Pattison, ed.), Marcel Dekker, Inc., New York, 1968, pp. 25-29.
3. R. H. Potts and V. J. Muckerheide, in Fatty Acids and Their Industrial Applications (E. S. Pattison, ed.), Marcel Dekker, Inc., New York, 1968, pp. 38-44.

4. R. H. Potts and V. J. Muckerheide, in *Fatty Acids and Their Industrial Applications* (E. S. Pattison, ed.), Marcel Dekker, Inc., New York, 1968, pp. 29-38.
5. A. Davidsohn and B. M. Milwidsky, *Synthetic Detergents*, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.
6. Dan C. Tate, Tall Oil, in *Encyclopedia of Chemical Technology*, Vol. 19, 2nd ed (A. Standen, ed.), John Wiley & Sons, Inc., New York, 1969, pp. 614-629.
7. L. G. Zachary, H. W. Bajak, and F. J. Eveline, Tall Oil and Its Uses, Tall Oil Products Division of Pulp Chemicals Association, New York, 1965, Chaps. 1 and 2.
8. I. A. Pearl, *The Chemistry of Lignin*, Marcel Dekker, Inc., New York, 1967, pp. 4-5.
9. D. W. Goheen, D. W. Glennie, and C. H. Hoyt, Lignin, in *Encyclopedia of Chemical Technology*, Vol. 12, 2nd ed. (A. Standen, ed.), John Wiley & Sons, Inc., New York, 1967, pp. 361-381.
10. F. A. Norris, in *Bailey's Industrial Oil and Fat Products* (D. Swern, ed.), John Wiley & Sons, Inc., New York, 1964, Chap. 15.
11. D. Swern, in *Bailey's Industrial Oil and Fat Products* (D. Swern, ed.), John Wiley & Sons, Inc., New York, 1964, pp. 8-11.
12. T. P. Hilditch and P. N. Williams, *The Chemical Constitution of Natural Fats*, 4th ed., John Wiley & Sons, Inc., New York, 1964, p. 488.
13. T. P. Hilditch and P. N. Williams, *The Chemical Constitution of Natural Fats*, 4th ed., John Wiley & Sons, Inc., New York, 1964, pp. 72-73.
14. K. P. Schroeder, *J. Am. Oil Chemists' Soc.*, 33, 565-568 (1956).
15. E. F. Hill, G. R. Wilson, and E. C. Steinle Jr., *Ind. Eng. Chem.*, 46, 1917-1921 (1954).
16. H. Bertsch, H. Reinheckel, and K. Haage, *Fette, Seifen, Anstrichmittel*, 71, 357-362 (1969).
17. J. D. Richter and P. J. Van den Berg, *J. Am. Oil Chemists' Soc.*, 46, 155-166 (1969).
18. R. S. Klonowski, T. W. Findley, C. M. Josefson, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, 47, 326-328 (1970).
19. K. S. Markley, *Fatty Acids*, 2nd ed., Interscience Publishers, Inc., New York, 1961, pp. 757-984.
20. A. C. Bell and W. G. Alsop, U.S. Pat. 2,478,354 (1949), to Colgate-Palmolive Co.
21. M. H. Ittner, U.S. Pat. 2,496,328 (1950), to Colgate-Palmolive Co.
22. H. A. Goldsmith, *Chem. Rev.*, 33, 257 (1943).
23. L. M. Schenk, U.S. Pat. 3,004,049 (1961), to General Aniline & Film Corp.
24. R. G. Bistline, E. S. Rothman, S. Serota, A. J. Stirton and A. N. Wrigley, *J. Am. Oil Chemists' Soc.*, 48, 657-660 (1971).
25. A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, 34, 39 (1957).
26. W. B. Satkowski and C. G. Hsu, *Ind. Eng. Chem.*, 49, 1875 (1957).
27. T. P. Matson, *Soap Chem. Specialties*, 39, 52 (1963).

28. W. M. Linfield, in Cationic Surfactants (E. Jungermann, ed.), Marcel Dekker, Inc., New York, 1970, Chap. 2.
29. R. H. Potts and R. S. Smith, U.S. Pat. 2,808,426 (1957), to Armour & Co.
30. R. H. Potts, U.S. Pat. 3,299,117 (1967), to Armour & Co.
31. R. H. Potts and C. W. Christensen, U.S. Pat. 2,314,894 (1943),
32. H. L. Sanders and M. Nassau, Soap Chem. Specialties, 36 (1), 57 (1960).